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Note

Dependence of the Crystal Structure Parameters on the Size of the Structural Units in Some Isomorphous / Isostructural Series

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Previous studies of kieserite analogues and also other systems (Tutton's salts, alums and β-K_2SO_4 isomorphs) have shown that in a series of isostructural/isomorphous compounds the unit-cell parameters and volumes vary linearly with the effective ionic radii (the 'size') of the structural units. This is in line with the results of Shannon (*Acta Cryst.* **A32** (1976) 751–767). Somewhat unexpectedly, other important parameters of the crystal structure, such as fractional atomic co-ordinates, exhibit systematic variations as well. An attempt is made to reveal the reasons that are at the origin of this finding.

INTRODUCTION

The crystal structures of quite a number of members of different isostructural/isomorphous series are known. Particular attention has been paid so far to the structure determination and refinement of various Tutton's salts,[1–8] alums,[9–17] kieserite group isomorphs,[18–20] and β-K_2SO_4 type isomorphs[21–23] by the methods of X-ray and neutron diffraction.

It has been shown that the unit-cell parameters within a series of related compounds depend on the size (*i.e.* effective ionic radii) of the constituent ions.[1,9,24,25] This behaviour has been proven to be highly statistically significant,[9,23] but it may also be self-explanatory: within an isomorphous

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group of compounds, the larger the ions – the larger the cell parameters. Intuitively, it may seem that the general structure of a given isostructural family can be described as the structure of any particular member, while the structures of other members are simply homothetic images of this 'parent' structure (of course, the parent may be chosen quite arbitrarily). This notion is quite useful. It probably underlies the reasoning that motivates crystallographers to simply substitute the fractional atomic coordinates from an isomorph with the determined structure, as the 'first guess' coordinates of the isomorph whose structure is to be determined, and then make full refinement.

No matter how useful it is, this concept is a rather rough one. Contrary to what intuition suggests, experience shows that the fractional atomic coordinates within a family of isostructural compounds often exhibit systematic variations with the size (*i.e.* effective ionic radius[26]) of the structural units.[21,23,27] This is illustrated in Table I for the fractional atomic coordinates in the kieserite family of crystals. The situation is similar in the case of the β-K_2SO_4 isomorphs.[21,23]

Previous studies revealed that both cell parameters and fractional atomic coordinates in the above two isostructural families vary *linearly* with the size of the structural units.[1,9,24,25,27] The regression coefficients are rather high in most cases. A simple explanation for this finding will be offered in this paper.

TABLE I

Variation in the fractional co-ordinates as a function of the cation size for the kieserite family of crystals, $M^{II}SO_4H_2O$ (values for effective ionic radii taken from Shannon;[26] x and z fractional coordinates for both S and O3 are 0 and 1/2, respectively; data deviating from the idealised trend are marked with an asterisk)

Fractional coordinate	$R(Mn^{2+})$ = 83 pm	$R(Fe^{2+})$ = 78 pm	$R(Co^{2+})$ = 74.5 pm	$R(Zn^{2+})$ = 74 pm	$R(Ni^{2+})$ = 69 pm
y(S)	0.14983 (7)	0.15307 (9)	0.15371 (8)	0.15510 (14)	0.15667 (7)
x(O1)	0.1679 (2)	0.1697 (2)	0.1725 (2) *	0.1714 (3)	0.1724 (2)
y(O1)	0.0398 (2)	0.0429 (2)	0.0429 (2) *	0.0440 (3)	0.0469 (2)
z(O1)	0.3926 (2)	0.3985 (3)	0.4004 (2) *	0.3997 (3)	0.4031 (2)
x(O2)	0.0944 (2)	0.0956 (2)	0.0969 (2)	0.0993 (3)	0.1032 (2)
y(O2)	0.2615 (2)	0.2683 (2)	0.2667 (2) *	0.2687 (3)	0.2697 (2)
z(O2)	0.1574 (2)	0.1560 (2)	0.1540 (2) *	0.1556 (3)	0.1548 (2)
y(O3)	0.6485 (2)	0.6444 (3)	0.6383 (3)	0.6380 (5)	0.6316 (2)

THE (HYPOTHETICAL) MXY_6 CUBIC ISOSTRUCTURAL SERIES

Let us consider an MXY_6 series of compounds. For simplicity, it will be assumed that the compounds are cubic and crystallise with the $Pm3m$ space group. For the present purpose, it is totally irrelevant whether such a series really exists*; in order to prevent possible criticism from the cautious reader, we will deal with a hypothetical one. The structure is such that the metal cations occupy the vertices of the elementary cube and the octahedral anion is placed in the centre of the cube. Using the simplest choice for the co-ordinate origin and denoting $R(X–Y) = d$, one may infer by simple inspection (cf. Fig. 1) the following statements for the 15 atoms defining the elementary cube of edge a**:

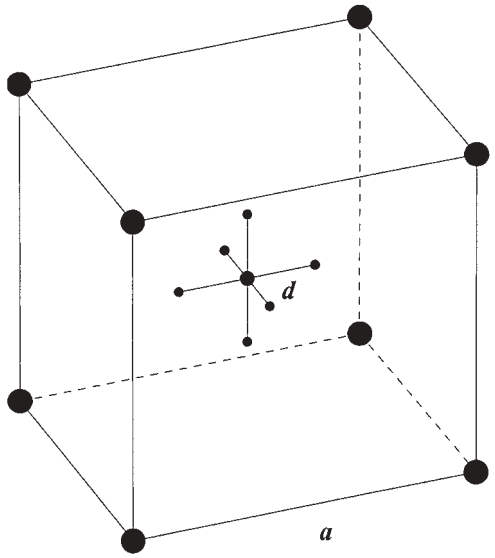

Figure 1. The unit cell of the MXY_6 isomorphs: large circles – M cations; medium circle – X atom; small circles – Y atoms; a is the cell edge, and d – the X-Y distance.

- fractional co-ordinates of metal cations M are 0, 0, 0 and their translational images (1, 0, 0 ; 0, 1, 0 *etc.*);
- fractional co-ordinates of atom X are 0.5, 0.5, 0.5;
- fractional co-ordinates of the six Y atoms are $0.5 + d/a$, 0.5, 0.5 and their images generated by application of S_6 operation about the C_3 axis.

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* One may speculate with the $M^{II}SiF_6$ series, where $M^{II} = Mg^{2+}$, Ca^{2+}, Sr^{2+}, Ba^{2+} or $M^{II} = V^{2+}$, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} ...

** However, there is a total of only 8 atoms (*i.e.* one formula unit) per unit cell.

Two points are of importance:

– An increase in the size of the metal cation M will result in a linear increase of the unit cell edge;

– The X–Y bond-length within the given XY_6 group*** is practically indifferent to the rest of the structure (that is, d is a constant to the first approximation).

Since the co-ordinates of M and X atoms are fixed by symmetry, the only variable are the fractional coordinates of Y atoms. Let one atom be taken as a representative (since all other Y atoms are equivalent by symmetry), its x fractional coordinate being $0.5 + d/a$. It is clear that this fractional coordinate will decrease as the size of M increases (this is a consequence of the fact that a increases linearly with M).

If a varies within certain limits throughout the series (say $a = a_0 + \Delta a$, where a_0 is the unit cell edge in the parent compound and the variation Δa is not very large, as is usually the case for most isostructural series), the dependence of the fractional coordinate on the cell edge takes the form:

$$x(\mathrm{Y}) = 0.5 + \frac{d}{a_0 + \Delta a}\,.$$

In terms of differential calculus, it is easy to prove that this (hyperbolic) dependence may be well approximated by the Taylor expansion up to the linear term:

$$x(\mathrm{Y}) \approx 0.5 + \frac{d}{a_0} - \frac{d\Delta a}{a_0^2} = 0.5 + \frac{d}{a_0}\left(2 - \frac{a}{a_0}\right)$$

which is linear with respect to a. This analysis shows that, indeed, an explanation for the detected linear dependence of the fractional co-ordinates on the ion size may be offered, at least within the above approximations.

We turn now to more involved cases, where the atomic positions are not fixed by symmetry. Two different cases will be discussed:

i) Fractional co-ordinates of the centre of gravity of the structural units are constant throughout the series;

ii) Structural units are subject to shifts ('translations' and 'rotations') within the crystal in order to attain the minimum energy positions.

Case i resembles the example of the already discussed cubic MXY_6 series. Indeed, if the fractional co-ordinates of the centres of gravity are fixed,

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*** It is an empirical fact that most chemical species (not only XY_6 groups) may be considered as being rigid. This is an excellent presumption for a group of isostructural compounds, where only minor changes in the geometry (*i.e.* bond-lengths and angles) are expected.

then increasing the radius of M will have the same effect on the atoms away from the centre of gravity as described above.

Case ii is probably encountered in the mentioned kieserite and β-K_2SO_4 families. The shifts ('translations') of the polyatomic anions are monitored through the changes in the fractional co-ordinates of the central atom (S) and they are also systematic (*cf.* Table I). This systematic trend is easily explained if one recalls the importance of the electrostatic potential in the crystal energy minimising: the charge density of the metal cations varies regularly with the cation size, and this induces regular variation in the position/orientation of the polyatomic anions.

The occasional deviations from the idealised trend (*cf.* Table I), even for groups of relatively simple compounds (there are only 6 non-equivalent atoms in the structure of kieserite compounds), show that the above approach is somewhat oversimplified. In the case of more complex compounds (*e.g.* in Tutton's salts, where one may find at least 16 non-equivalent atoms), it seems difficult to establish a statistically significant correlation. The chemical nature (*i.e.* electron configuration) of the structural units was completely ignored in the above approach, and it should not be in a really sophisticated one. Anyway, the proposed approach and the offered explanation may be useful as a step away from the non-realistic picture of members in an isostructural family of crystals, viewed as homothetic images of one another.

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REFERENCES

1. V. Petruševski and S. Aleksovska, *Croat. Chem. Acta* **64** (1991) 577–583 (and references cited therein).
2. H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.* **20** (1966) 659–662.
3. H. Montgomery, *Acta Crystallogr.* **C40** (1984) 14–15.
4. B. E. F. Fender, B. N. Figgis, and J. B. Forsyth, *Aust. J. Chem*. **39** (1986) 1023–1028.
5. E. N. Maslen, S. C. Ridout, and K. J. Watson, *Acta Crystallogr.* **B44** (1988) 96–101.
6. E. N. Maslen, S. C. Ridout, K. J. Watson, and F. H. Moore, *Acta Crystallogr.* **B44** (1988) 409–412.
7. B. N. Figgis, E. S. Kucharski, and J. B. Forsyth, *Acta Crystallogr.* **C47** (1991) 419–421.
8. T. H. Tahirov, T.–H. Lu, C.–C. Huang, and C.–S. Chung, *Acta Crystallogr.* **C50** (1994) 668–669.
9. V. Petruševski and S. Aleksovska, *Croat. Chem. Acta* **67** (1994) 221–230 (and references cited therein).
10. R. S. Armstrong, J. K. Beattie, S. P. Best, B. W. Skelton, and A. H. White, *J. Chem. Soc. Dalton Trans*. (1983) 1973–1975.

11. M. Brorson and M. Gajhede, *Inorg. Chem*. **26** (1986) 2109–2112.
12. R. S. Armstrong, J. K. Beattie, S. P. Best, G. P. Braithwaite, P. Del Favero, B. W. Skelton, and A. H. White, *Aust. J. Chem*. **43** (1990) 393–398.
13. S. P. Best and J. B. Forsyth, *J. Chem. Soc. Dalton Trans*. (1990) 395–400.
14. S. P. Best and J. B. Forsyth, *J. Chem. Soc. Dalton Trans*. (1991) 1721–1725.
15. J. K. Beattie, S. P. Best, F. H. Moore, B. W. Skelton, and A. H. White, *Aust. J. Chem*. **46** (1993) 1337–1345.
16. S. P. Best, B. N. Figgis, J. B. Forsyth, P. A. Reynolds, and P. L. W. Treggena-Piggott, *Inorg. Chem*. **34** (1995) 4605–4610.
17. J. K. Beattie, S. P. Best, P. Del Favero, B. W. Skelton, A. N. Sobolev, and A. H. White, *J. Chem. Soc. Dalton Trans*. (1996) 1481–1486.
18. F. C. Hawthorne, L. A. Groat, M. Raudsepp, and T. S. Ercit, *N. Jb. Miner. Abh*. **157** (1987) 121–132.
19. M. Wildner and G. Giester, *N. Jb. Miner. Mh*. (1991) 296–306.
20. G. Giester and M. Wildner, *N. Jb. Miner. Mh*. (1992) 135–144.
21. S. Aleksovska, V. M. Petruševski, and Lj. Pejov, *Croat. Chem. Acta* **70** (1997) 1009–1019 (and references cited therein).
22. A. J. Morris, K. L. Kennard, F. H. Moore, G. Smith, and H. Montgomery, *Cryst. Struct. Comm.* **10** (1981) 529–532.
23. S. Aleksovska, S. C. Nyburg, Lj. Pejov, and V. M. Petruševski, *Acta Crystallogr.* **B54** (1998) 115–120.
24. O. Fukunaga and T. Fujita, *J. Solid Sate Chem*. **8** (1973) 331–338.
25. O. Knop and J. S. Carlow, *Can. J. Chem*. **52** (1974) 2175–2183.
26. R. D. Shannon, *Acta Crystallogr.* **A32** (1976) 751–767.
27. S. Aleksovska, V. M. Petruševski, and B. Šoptrajanov, *Acta Crystallogr.* **B54** (1998) 564–567.

SAŽETAK

Ovisnost parametara kristalne strukture o veličini strukturnih jedinica u nekim izomorfnim / izostrukturnim nizovima

Vladimir M. Petruševski i Slobotka Aleksovska

Prijašnja proučavanja kieseritu analognih spojeva i također drugih sistema (Tuttonovih soli, alauna i s β-K_2SO_4 izomorfnih spojeva), pokazala su da u nizu izostrukturnih / izomorfnih spojeva, parametri i volumeni jediničnih ćelija variraju linearno s efektivnim ionskim radijusima (»veličinom«) strukturnih jedinica. To je u skladu sa Shannonovim rezultatima (*Acta Cryst*. **A32** (1976) 751–767). Donekle neočekivano, i drugi važni parametri kristalne strukture, na pr. frakcijske atomske koordinate, također sistematski variraju. Pokušali smo otkriti razloge za to.